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Results of amine plant operations from 30 wt% and 40 wt% aqueous MEA testing at the CO_2 Technology Centre Mongstad

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Abstract

An amine plant campaign has been performed at the CO_2 Technology Centre Mongstad applying the aqueous 30 wt% and 40 wt% monoethanolamine (MEA) solvent systems for treatment of flue gas from a combined heat and power (CHP) plant. CHP flue gas flow rates were ranging from about 40.000 Sm^3/h to 60.000 Sm^3/h and the CO_2 content was about 3.5 vol%.

Minimum specific reboiler duties (SRD) of respectively 4.0 MJ/kg CO_2 and 3.7 MJ/kg CO_2 were obtained for the aqueous 30 wt% MEA solvent system without and with the addition of anti-foam solution. A minimum SRD of 3.4 MJ/kg CO_2 was obtained for the aqueous 40 wt% MEA solvent system. Lower SRD and absorber liquid to gas (L/G) ratios were obtained with higher concentration MEA solvents.

Increased absorber packing heights resulted in lower SRD. Variation in flue gas supply flow rates and corresponding variations in solvent flow rates, i.e. constant L/G ratios, did not yield any significant variations in SRD. Decreased flue gas supply temperatures resulted in lower SRD.

For any future large scale post-combustion capture (PCC) amine plant, engineering aspects such as the flue gas supply temperature and instrumentation monitoring CO_2 content in the flue gas must be evaluated to avoid the chemical equilibrium pinch behavior. Engineering and environmental aspects related to the use of anti-foam solutions for future large scale PCC amine plants must also be considered.

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Keywords: Amine plant operations; 30 wt% monoethanolamine; 40 wt% monoethanolamine

1. Introduction

The CO_2 Technology Centre Mongstad (TCM DA) is the one of the world's largest and most advanced facilities for testing and improving CO_2 capture technology. The facility enables vendors of suitable amine formulations and other post-combustion capture processes to test their process, collecting performance data to support full-scale design. The vendors can then anticipate the associated performance and operating costs of their amine formulations and capture processes. As a result, one of the main objectives of TCM DA is to investigate and demonstrate the flexibility of post-combustion amine based solvent systems with respect to load changes, variations in flue gas composition, variations in amine plant operations and solvent system compositions in order to achieve optimal and environmentally safe operating conditions. The flue gas utility system allows for flue gas supplies with varying temperatures, flow rates, and CO_2 content and also different types of flue gases with various trace components from either a combined heat and power (CHP) plant or a refinery catalytic cracker. In the CHP plant, the natural gas is combusted in a gas turbine and the flue gas content and characteristics are similar to those of a combined cycle gas turbine (CCGT) power plant. The amine plant at TCM DA is a highly flexible and well instrumented generic amine plant, designed and constructed by Aker Solutions, aimed to accommodate a variety of technologies with capabilities of treating flue gas streams of up to 60.000 Sm^3 per hour. The flexibility of the amine plant allows for handling of a wide range of flue gas flow rates, temperatures, and CO_2 content in the flue gas, and also a wide range of various operational parameters, i.e. solvent flow rates, absorber packing heights, stripper pressures, reboiler heat duties, lean amine and cross heat exchanger duties, absorber water wash temperatures and flow rates with or without acid injections, anti-foam solution injections, etc. [1, 2]

The campaign described in the current paper was conducted at TCM DA in the period December 2013 to February 2014 as a part of Aker Solutions' test period. In general, during the campaign the aqueous 30 wt% monoethanolamine (MEA) solvent system was applied treating the flue gas from the CHP plant. The primary purposes and goals of the campaign were:

- Generate results from CHP plant operations with CO_2 capture
- Generate an independently verified TCM DA amine plant base case while treating CHP plant flue gas with the aqueous 30 wt% MEA solvent system [3, 4]
- Investigate the performance potential of higher MEA concentration solvents
- Verify design capacities and flexibilities of the TCM DA amine plant and specific functionalities
- Gain better understanding of scale-up, performance, and emission aspects and transient operations of the TCM DA amine plant
- Verify and improve process simulation models
- Test and improve various online analyser for emission monitoring [5]
- Scientific dissemination of some results

These purposes and goals are aimed for gaining experience and knowledge for future large scale carbon capture and storage (CCS) projects.

This work is part of a continuous effort of gaining better understanding of the performance potential of the non-proprietary aqueous MEA solvent system, conducted by TCM DA and its affiliates and owners, in order to test, verify, and demonstrate CO_2 capture technologies. [3, 4, 5] The purpose of the current work is to provide results of various operational conditions of the TCM DA amine plant, and hence demonstrating some capacities, flexibilities, and performances of the plant while treating CHP flue gases.

2. Testing Philosophy

An overview of the TCM DA amine plant has been given elsewhere. [3, 4, 5]

The test philosophy during the current campaign was to adjust one operational parameter at a time, e.g. the solvent flow rate, the gas flow rate, etc., whilst subsequently allowing the amine plant to reach steady-state operations and simultaneously manually controlling the CO_2 capture rate to a specific value. The CO_2 capture rate was controlled to about 85% for most of the campaign by manually adjusting the reboiler steam flow rate. The response time of the amine plant was up to about 3 hours, depending on the varied operational parameter. The plant was operated for at least an additional 3 hours of steady-state operations after an operational parameter change before the plant was considered to provide representative process values. Any solvent sampling for laboratory analysis was conducted once representative process values were obtained. Certain transient operations were conducted during the campaign, and the aforementioned test philosophy was adapted in order to accommodate such operations. During Base-Case testing, as described elsewhere [3, 4], the amine plant was operated at steady-state operations for about 1 week.

Table 1 provides the main operational parameters and ranges adjusted during the campaign. Approximately 150 different operating conditions were conducted during the campaign, and the results of some of these are presented in the current work.

Table 1: MEA campaign overview

Adjusted operational parameter		Range
Flue gas flow rate	Sm^3/h	30.000 - 60.000
Flue gas temperature	°C	20 – 50
Flue gas CO_2 concentration	vol%	3.2 – 11.0
Lean solvent flow rate	m^3/h	30 – 150
Lean solvent temperature	°C	20 – 45
L/G ratio	kg liquid / kg gas	0.5 – 2.5
CO_2 capture rate	%	60 – 95
MEA concentration	wt%	25 – 45
Absorber packing height	m	12 – 24
Stripper pressure	bara	1.9 – 2.5
Stripper reboiler duties	MW	2.5 – 6

The calculations procedures for the various performance indices presented in the current work are as described by Thimsen et al. [3] and Hamborg et al. [4].

3. Chemicals

MEA [CAS: 141-43-5] was supplied by AkzoNobel, and was diluted to a desired solvent concentration by addition of demineralized water. Anti-foam solution was supplied from KCC Basildon.

4. Results and Discussion

4.1. Mass recovery and MEA solvent concentrations

The total mass and CO_2 mass recovery also referred to as the total mass and CO_2 mass balances, for the complete campaign, were determined as described by Thimsen et al. [3] and displayed in Figure 1. The total mass recovery is, as expected, close to 100% during the complete campaign. The CO_2 mass recovery is however scattered, and this may be attributed to inadequate instrumentation for monitoring of the CO_2 gas phase concentrations in the flue gas supply and depleted flue gas. The gas phase concentrations of CO_2 in the flue gas streams were monitored by the installed Fourier transform infrared spectroscopy (FTIR) analyzer, and accuracy and precision challenges with respect to this FTIR analyzer setup has been described by elsewhere. [4] The scattering of the CO_2 mass recovery displayed in Figure 1 leads to uncertainties in the CO_2 capture rates, whereas the specific thermal use, as derived in the current work, is independent of the FTIR analyzer system. [4]

The MEA solvent concentrations, based on sampling and laboratory analysis of the lean amine, are displayed in Figure 2. The MEA solvent concentration was maintained at about 30 wt% during most of the campaign, and was increased to above 40 wt% towards the end. The MEA solvent water balance was maintained by adjusting the depleted flue gas temperature to the flue gas supply temperature, and, if necessary, addition of demineralized water to the MEA solvent. Due to the rapid change of operational parameters and conditions and additional time consuming sampling and laboratory analysis, the MEA solvent concentration could not be maintained at constant values throughout the campaign.

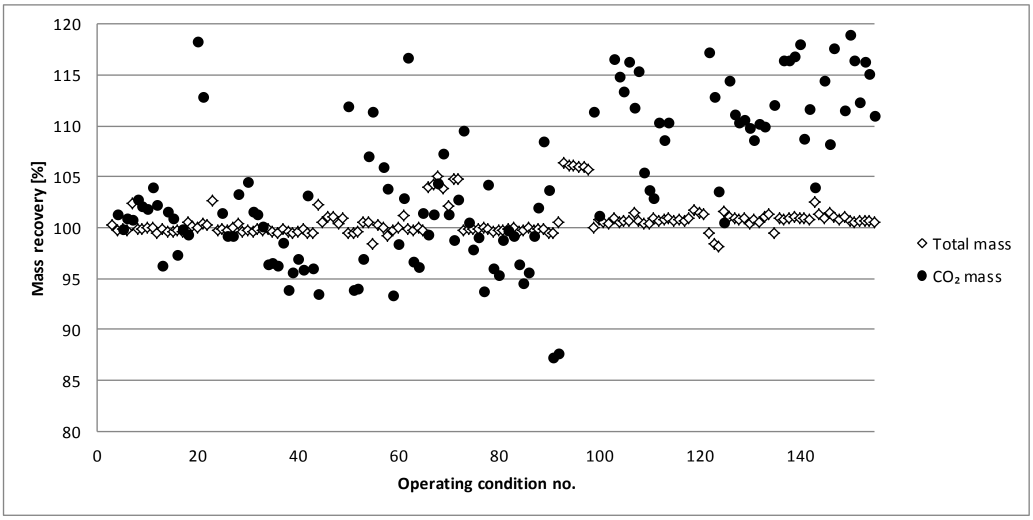

Figure 1: Total and CO_2 mass recovery at various operating conditions

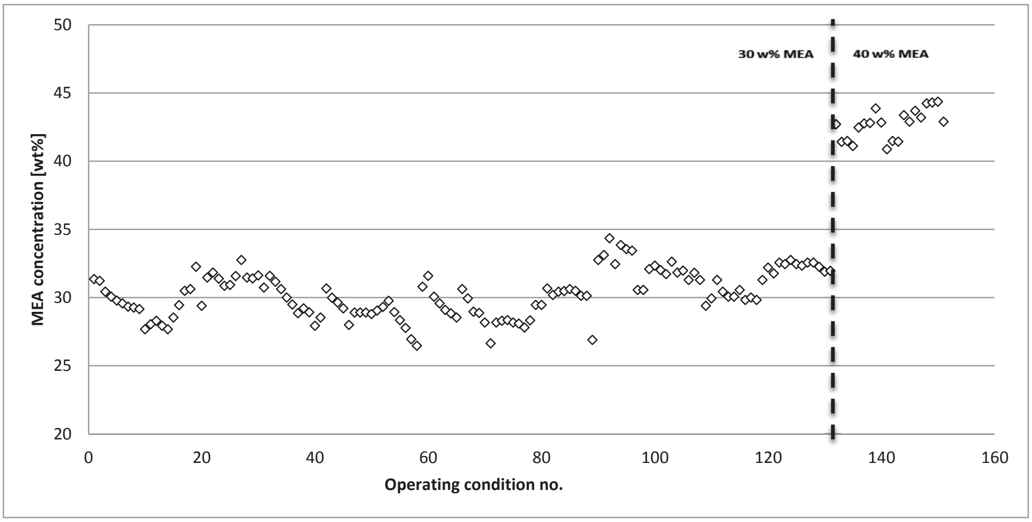

Figure 2: MEA concentrations at various operating conditions

4.2. Overall energy performances

Figure 3 displays the specific reboiler duties (SRD) for the aqueous 30 wt% MEA solvent system with and without the use of anti-foam solutions. The plant was operated with 24 meters of absorber packing heights, 1.9 bara stripper pressure, and a flue gas flow rate of about 47.000 Sm^3/h at 25 °C. The CO_2 capture rate was kept at about 85 %. The results in Figure 3 show a clear minimum in the SRD of about 4.0 MJ/kg CO_2 at a lean amine loading of about 0.25 for operations without anti-foam solutions added. Results refer to Base-Case testing as presented elsewhere [4] provided a SRD of 4.1 MJ/kg CO_2 and is displayed in Figure 3. For operations with addition of anti-foam solutions, the minimum SRD is shifted towards lower lean CO_2 loadings, and the cause for this behavior is described later. The minimum SRD for these operations with anti-foam addition may have not been achieved. The lean amine CO_2 loading can be assumed closely proportional to the MEA solvent circulation rate, assuming steady-state plant operations, and in these specific cases solvent circulation rates approached the minimum achievable due to solvent pump limitations. Lower solvent flow rates could have been achieved with the use of the solvent filtration system however this was not tested during operations with addition of anti-foam solutions. The minimum SRD obtained for operations with anti-foam solutions added was approximately 3.7 MJ/kg CO_2.

Figure 4 displays the SRD for the aqueous 40 wt% MEA solvent system. The plant was operated with 24 meters of absorber packing heights, 1.9 bara stripper pressure, and a flue gas flow rate of about 59.000 Sm^3/h at 25 °C. The CO_2 capture rate was kept at about 85 %. The results in Figure 4 show a minimum in the SRD of about 3.4 MJ/kg CO_2 at lean amine loadings ranging between 0.2 and 0.25. A batch of anti-foam solutions were added several days prior to these tests, and the effect of the anti-foam solution was likely present during these operating conditions.

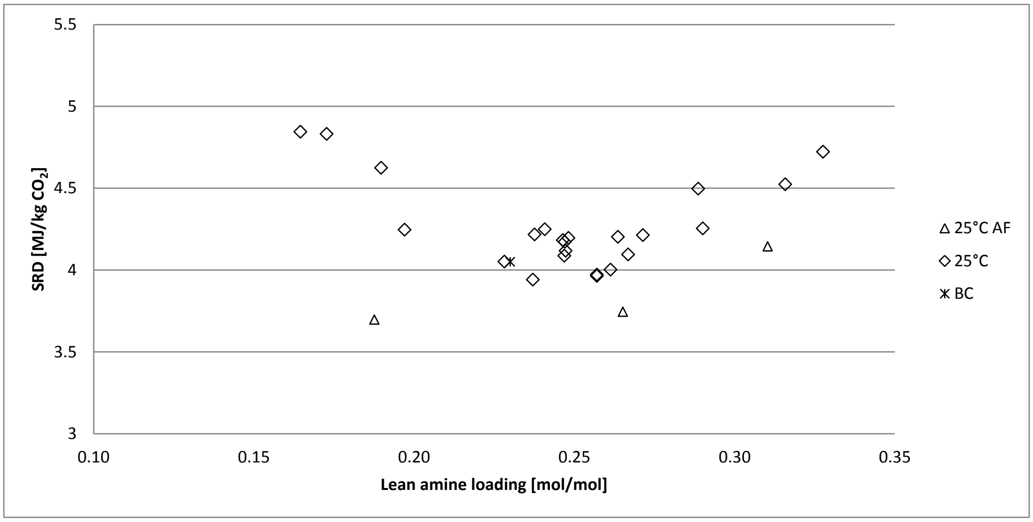

Figure 3: SRD for the 30 wt% aqueous MEA solvent system as a function of the lean amine CO_2 loading. AF indicates operations with anti-foam solutions injected into the aqueous MEA solvent system. BC indicates the Base-Case operation as in described by Hamborg et al. [4]

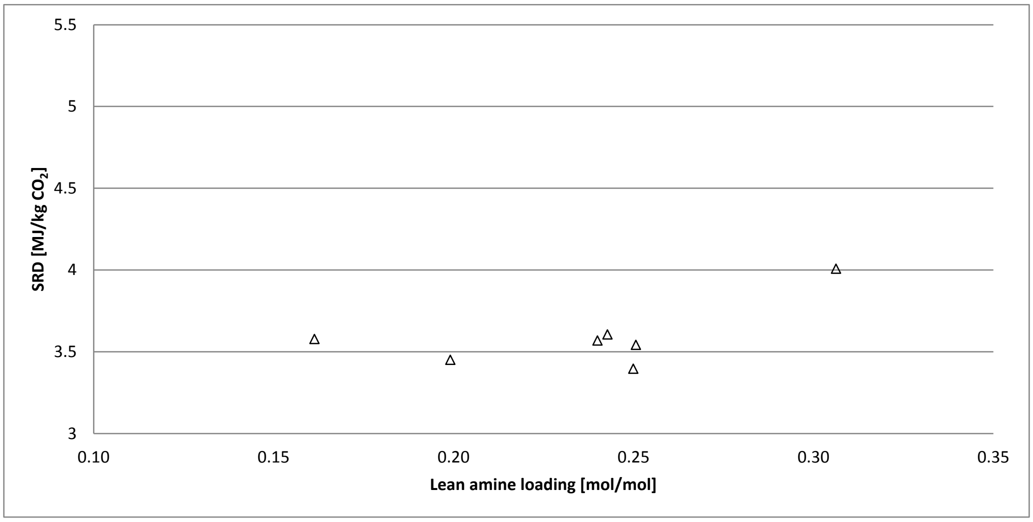

Figure 4: SRD for the 40 wt% aqueous MEA solvent system as a function of the lean amine CO_2 loading.

Figure 5 displays a comparison of the results presented in Figure 3 and Figure 4 as a function of the ratio of solvent flow rate to the flue gas supply rate on mass basis (L/G ratio). Operations with the 40 wt% aqueous MEA solvent system clearly provide lower values of the SRD and L/G ratios. The use of 40 wt% or higher MEA concentrations must however be considered with respect to higher solvent degradation rates, as described by Morken et al. [5], and possible material corrosion rates. The latter is however irrelevant for the TCM DA amine plant as it is constructed primarily of high grade stainless steel and polypropylene plastic material for absorber lining. The metal ion concentrations were monitored during the MEA campaign, and no significant increase in ion concentration was observed for 40 wt% operations.

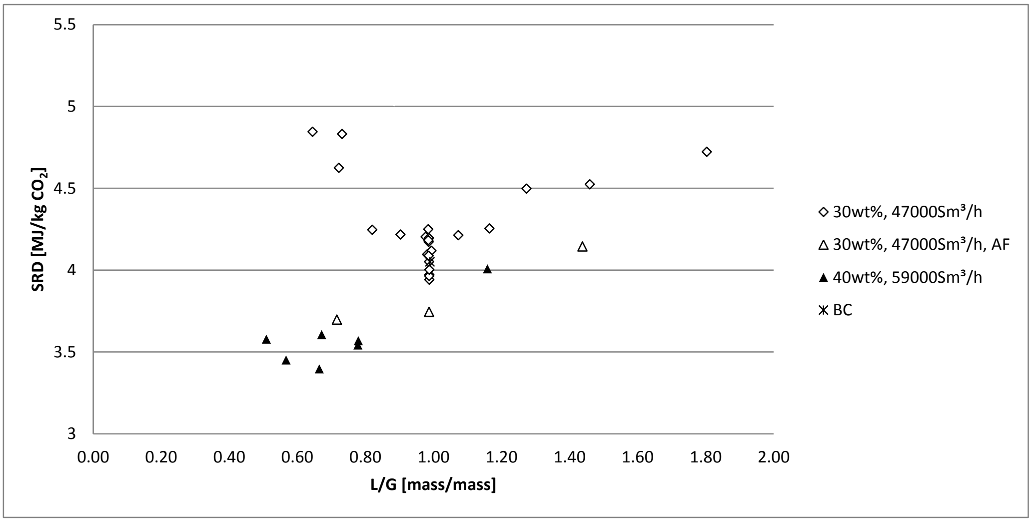

Figure 5: SRD for the 30 wt% and 40 wt% aqueous MEA solvent system as a function of L/G ratios

4.3. Effects of absorber packing heights

Figure 6 displays the effects of absorber packing heights. The SRD obtained with 24 meters of absorber packing heights of about 4.0 MJ/kg CO_2 are lower than those of 18 meters of about 4.5 MJ/kg CO_2. The plant was operated at 1.9 bara stripper pressure and a flue gas flow rate of about 47.000 Sm^3/h at 25 °C. The CO_2 capture rate was kept at about 85 %.

It is well known that MEA is considered an amine with a relatively high kinetic reaction rate towards CO_2, and equilibrium conditions could be expected in the absorber bottom section. Solvent sampling and laboratory analysis resulted in rich solvent CO_2 loadings of about 0.44 and 0.48 for respective 18 meters and 24 meters of absorber packing heights, whereas the expected CO_2 equilibrium loading for the aqueous MEA system was approximately 0.50. Preliminary simulation work has indicated that it is most likely the kinetic rate which limits the approach to equilibrium in the test runs.

Similar trends, as displayed in Figure 6, were observed with the 40 wt% aqueous MEA solvent system at different absorber packing heights.

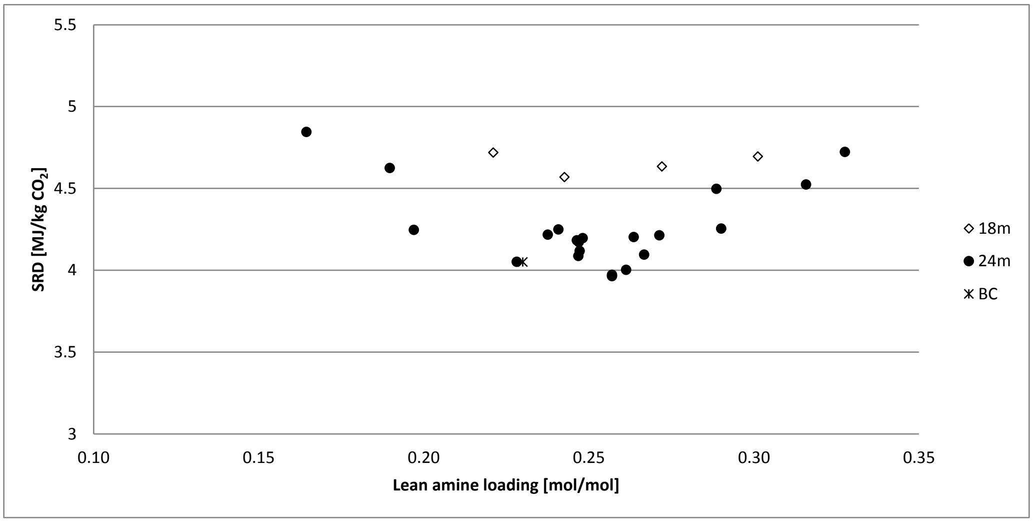

Figure 6: SRD for the 30 wt% aqueous MEA solvent system as a function of the lean amine CO_2 loading and absorber packing heights

4.4. Effect of flue gas supply flow rates

Figure 7 displays the effects of flue gas supply flow rates. The flue gas supply rate shows no significant effect on the SRD at specific lean amine loadings. The plant was operated with 24 meters of absorber packing heights, 1.9 bara stripper pressure, and a flue gas supply temperature of 25 °C. The CO_2 capture rate was kept at about 85 %. At specific lean amine loadings it can be assumed that the amine plant was operated at close to identical conditions for the various flue gas supply flow rates, except the correlated adjustment of the solvent flow rate. This would ideally create a constant L/G ratio for the various flue gas supply flow rates at a certain lean amine loading. The minor differences in the SRD between the various flue gas supply flow rates at a certain lean amine loading must therefore be attributed to normal operational variations of the various amine plant unit operations.

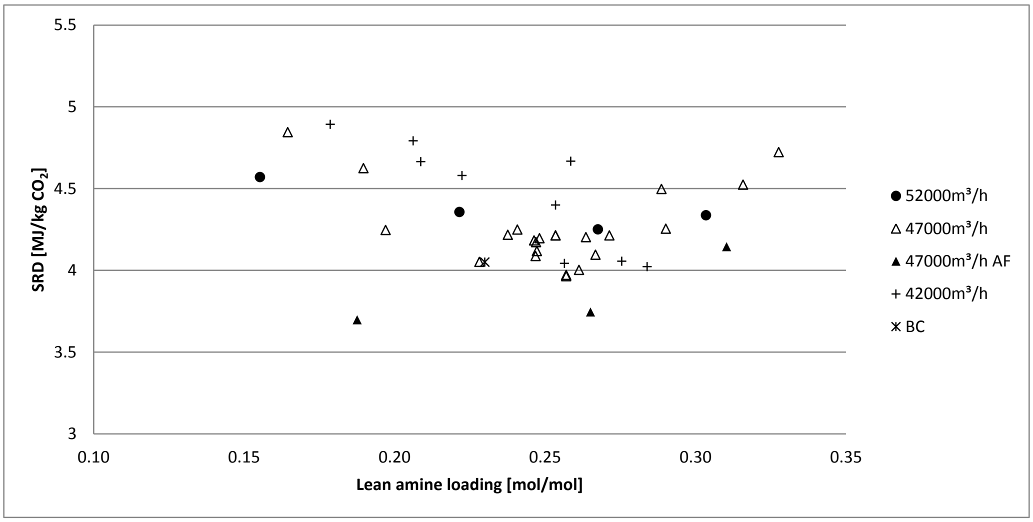

Figure 7: SRD for the 30wt% aqueous MEA solvent system as a function of the lean amine CO_2 loading and flue gas supply flow rates

4.5. Effect of flue gas supply temperatures

Increased SRD were observed when increasing the flue gas supply temperatures from 25 °C to about 50 °C. The SRD was determined to be about 4 MJ/kg CO_2 for the 30 wt% aqueous MEA solvent system at 25 °C flue gas supply temperatures, whereas the SRD was determined to be about 5.0 MJ/kg CO_2 for 50 °C flue gas supply temperatures. Some increase is expected due to the temperature dependent CO_2 vapor liquid equilibria behavior in the absorber bottom, leading to a lower rich amine loading at increased absorber bottom temperature, and the fact that the partial pressure of CO_2 is slightly lower in the flue gas supply stream of 50 °C than 20 °C leading to decreased mass transfer driving forces. However, the more important aspect encountered during these test conditions at elevated flue gas supply temperatures was chemical equilibrium pinching of the upper section of the absorber. This was encountered when the lean amine loading was not sufficiently low, i.e. the CO_2 equilibrium pressure in the lean amine solvent entering the absorber is close to or identical to the actual CO_2 partial pressure in the gas phase of the upper section of the absorber. At such conditions little mass transfer will occur in the upper section of the absorber, as mass transfer driving forces are low. In order to avoid such chemical equilibrium pinching, the lean amine loading would need to be lowered by e.g. increasing the stripper bottom temperature. Aspects around this are described further below.

The chemical equilibrium pinch behavior, as aforementioned, was encountered primarily as a result of the very low targeted depleted flue gas CO_2 partial pressure, as is a consequence of CO_2 capture from low partial CO_2 pressure CHP flue gases. Assuming flue gas supply CO_2 content of about 3.5 vol% and a corresponding partial pressure of about 35 mbara by assumption of ideal gas law behavior, the depleted flue gas CO_2 partial pressure would be about 5 mbara at 85 % CO_2 capture rate. In order to avoid and control such chemical equilibrium pinching behavior for any future large scale PCC amine plants in the upper section of the absorber, engineering considerations such as e.g. flue gas supply temperatures and sufficient instrumentation for monitoring of the CO_2 content in the depleted flue gas should be taken into account.

4.6. Effect of stripper behavior

Figure 8 and Figure 9 displays the effect of addition of anti-foam solution to the solvent. The effect of anti-foam solution addition on the SRD is more pronounced at lower lean amine loadings. The plant was operated at 1.9 bara stripper pressure and a flue gas flow rate of about 47.000 Sm^3/h at 25 °C. The CO_2 capture rate was kept at approximately 85 %.

Addition of anti-foam solutions showed no impact on the absorber temperature profile as displayed by Figure 8, but showed a considerable impact on the stripper temperature profile as displayed by Figure 9. The temperature values displayed in the Figure 8 and Figure 9 are the average value of four temperature sensors in the radial plane at each axial column position. For operations without anti-foam solutions, the stripper temperature profile shows relatively high temperatures in the upper section of the stripper of about 115 °C. It is well known that such will lead to excessive amounts of water vapor leaving the stripper and being further directed to the overhead condenser, which will lead to an unnecessarily high SRD. Upon analysis of the stripper temperature profiles in the radial plane and axial direction, it was concluded that transient channeling in the stripper bed occurred during operations without addition of anti-foam solution. This resulted in poor gas liquid distribution and contact, and condensation of the stripping gas and water vapor occurred in the overhead condenser rather than inside the stripper bed. Addition of anti-foam solution reduced the channeling behavior in the stripper, and well defined as expected stripper temperature profiles were obtained in the axial direction, as displayed by Figure 9, and minor temperature differences were observed in the radial plane. At these stripper operating conditions, only moderate amounts of water vapor, as defined by chemical phase equilibria, will leave the stripper and be further directed to the overhead condenser. This is defined as optimal stripper behavior. The exact cause of the observed transient steam channeling is not yet clearly understood, however it may be caused by the solvent foaming. Engineering aspects related to this and the use of anti-foam solutions for future large scale PCC amine plants must be considered. Environmental aspects of the use of anti-foam in such amine plants where the depleted flue gas may be emitted to air must also be considered.

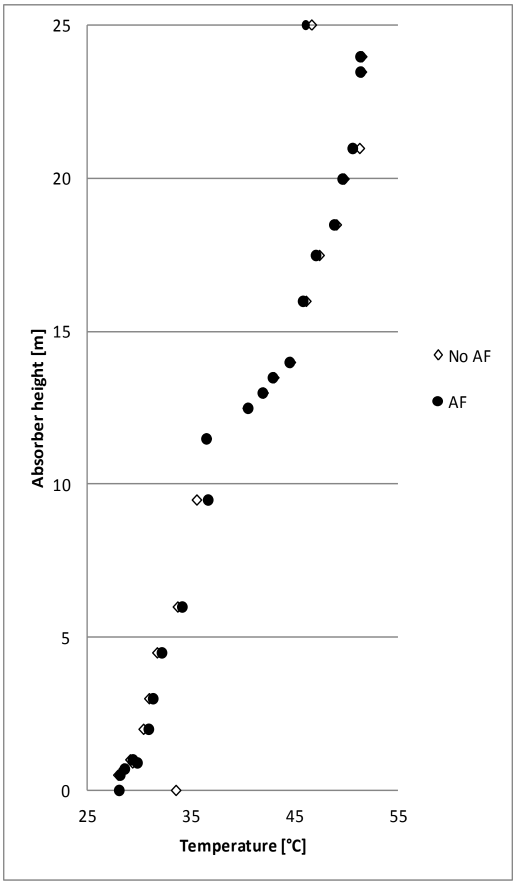

Figure 8: Absorber temperature profile with and without antifoam

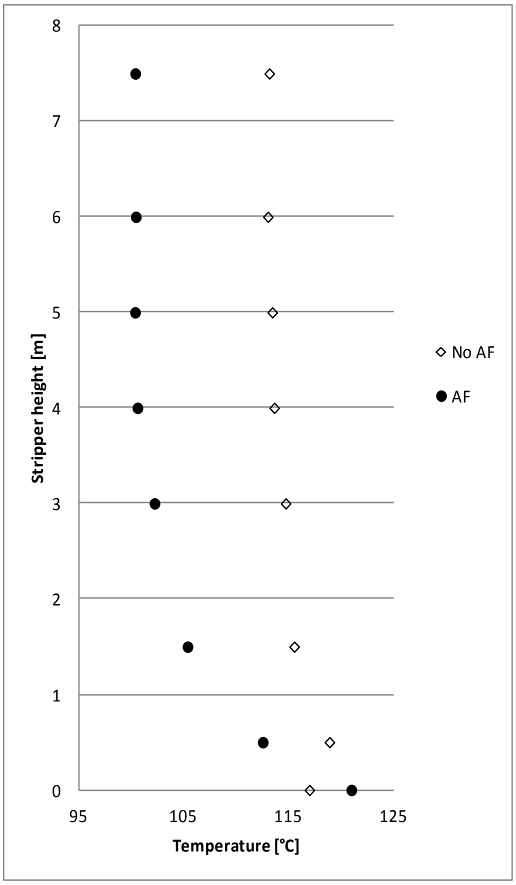

Figure 9: Stripper temperature profile with and without antifoam

5. Conclusion

A campaign has been performed in the amine plant at the CO_2 Technology Centre Mongstad applying the aqueous 30 wt% and 40 wt% MEA solvent systems for treatment of flue gas from a combined heat and power (CHP) plant. CHP flue gas flow rates were ranging from about 40.000 Sm^3/h to 60.000 Sm^3/h and the CO_2 content was about 3.5 vol%.

Minimum steam reboiler duties (SRD) of respectively 4.0 MJ/kg CO_2 and 3.7 MJ/kg CO_2 were obtained for the aqueous 30 wt% MEA solvent system without and with addition of anti-foam solution. Minimum SRD of 3.4 MJ/kg CO_2 was obtained for the aqueous 40 wt% MEA solvent system. Lower SRD and absorber liquid to gas (L/G) ratios could be obtained with the higher concentration MEA solvents.

Increased absorber packing heights resulted in lower SRD. Variation in flue gas supply flow rates and corresponding variations in solvent flow rates did not yield any significant variations in SRD. Decreased flue gas supply temperatures resulted in lower SRD, as rich amine loadings increased and chemical equilibrium pinch behavior in the upper section of the absorber was limited.

Engineering aspects such as flue gas supply temperatures and instrumentation for gas phase monitoring of the CO_2 flue gas contents must be considered for any future large scale PCC amine plant in order to avoid chemical equilibrium pinch behavior during treatment of CHP flue gases. Engineering and environmental aspects related to the use of anti-foam solutions for future large scale PCC amine plants must also be considered.

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